PATENT COOPERATION TREATY

PCT

From the INTERNATIONAL BUREAU

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

Assistant Commissioner for Patents
United States Patent and Trademark Office
Box PCT
Washington, D.C.20231
ÉTATS-UNIS D'AMÉRIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 18 November 1999 (18.11.99)	
International application No. PCT/NO99/00008	**Applicant's or agent's file reference** P9815
International filing date (day/month/year) 11 January 1999 (11.01.99)	**Priority date** (day/month/year) 13 March 1998 (13.03.98)
Applicant FUGLERUD, Terje et al	

1. The designated Office is hereby notified of its election made:

[X] in the demand filed with the International Preliminary Examining Authority on:

04 October 1999 (04.10.99)

[ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was

[ ] was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO
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1211 Geneva 20, Switzerland

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Authorized officer

F. Baechler

Telephone No.: (41-22) 338.83.38

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WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
B01J 21/06, C01C 1/04

A1

(11) International Publication Number: WO 99/46038

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(21) International Application Number: PCT/NO99/00008

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(30) Priority Data:
19981118 13 March 1998 (13.03.98) NO

(71) Applicant *(for all designated States except US)*: NORSK HYDRO ASA [NO/NO]; N–0240 Oslo (NO).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: FUGLERUD, Terje [NO/NO]; Snarveien 1, N–3925 Porsgrunn (NO). SKAUGSET, Per, Torbjørn [NO/NO]; Borgeåsen Terrasse 15, N–3911 Porsgrunn (NO).

(74) Agent: JOHNSEN, Venche, Høines; Norsk Hydro asa, N–0240 Oslo (NO).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: CATALYST FOR THE SYNTHESIS OF AMMONIA FROM HYDROGEN AND NITROGEN

(57) Abstract

The present invention relates to a catalyst for the synthesis of ammonia from hydrogen and nitrogen consisting of iron oxides and promoters where the promoters comprise oxides of both cobalt and titanium in addition to Al, K, Ca and Mg oxides, and where the concentration of cobalt is between 0.1 % and 3.0 % by weight of metal and the concentration of titanium is between 0.1 % and 1.0 % by weight of metal.

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Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

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CATALYST FOR THE SYNTHESIS OF AMMONIA FROM HYDROGEN AND NITROGEN

The present invention relates to a catalyst for the synthesis of ammonia from hydrogen and nitrogen.

The ammonia synthesis catalyst play an important role in the manufacture of ammonia. It effects both the economics and operating conditions of ammonia plants.

Industrial catalysts for ammonia synthesis must satisfy a number of requirements: high catalyst activity at the lowest possible reaction temperatures in order to take advantage of the favourable thermodynamic equilibrium at low temperatures, good resistance to poisoning by oxygen-, chlorine- and sulphur -containing compounds, long life and high mechanical strength.

In order to save energy the synthesis pressure has been steadily reduced from 250-350 bar to 80-150 bar during the last 30 years due to optimised operation of the synthesis loop made possible by new technology, especially for fabrication of the converter. Improvements in the front end has drastically reduced the content of catalyst poisons (oxygen- , sulphur- and chlorine-containing compounds) in the gas inlet to the converter. However, the drop in synthesis pressure necessitates a three- to four-fold increase in the catalyst volume. The demands upon the catalyst quality has also increased. Apparently small improvements in the catalyst activity may lead to major improvements of the operation of a modern ammonia synthesis loop.

The ammonia synthesis catalyst precursor, the unreduced catalyst, is manufactured by melting iron oxides, mainly magnetite, and oxides or carbonates of Al, K, Ca and Mg, the so-called promoters. The melting is performed in electrical furnaces at a temperature of above 1600 °C. The ratio Fe^{2+}/Fe^{3+} in the melt is normally in the range 0.5-0.75. The melt is then poured into metal trays where it solidifies and cools. The

solid precursor is then broken up, crushed and sieved to obtain the required grain size.

The precursor is reduced to active iron catalyst "in situ" in the ammonia synthesis converter or used to manufacture the prereduced catalyst by a complete reduction under optimised conditions in a prereduction reactor. This material is pyroforic, but after a skin oxidation of the active surface with oxygen, it can be handled safely in air at ambient temperatures.

The promoters mentioned above, containing Al, K,Ca and Mg, are essential for the formation of a large surface of iron in the reduced catalyst and for the kinetics of ammonia formation.
Since the development of the catalyst started, about 90 years ago, the concentration of these promoters have been optimised to obtain maximum activity and to meet the additional requirement mentioned above. Further improvements seem only possible by adding new promoters, or new combination of promoters.

Cobalt oxide has been used as such a new promoter.
From US patent 3839229 it is known an ammonia synthesis catalyst where cobalt oxide is used as a promoter. The catalyst consists essentially of a solid solution of iron oxide and cobalt oxide and said cobalt oxide is present in an amount of 5 to 10 percent by weight expressed as cobalt. In the catalyst there is further included a promoter selected from the group consisting of alumina, silica, zirconia, magnesia, lime (CaO),potassium oxide and rare earth metal oxides.

Another possible promoter is titanium oxide. Only few catalysts using this promoter have been previously described. S.A. Abdukadyrova et al. have in "Tr.Mosk.Khim.-Tekhnol.Inst. (1970),No.2,122-5", described that titanium oxide improves the thermal resistance but reduces the activity.

Titanium oxide used as a structural promoter is described by M. E. Dry et al in "Journal of Catalysis", 6, page:194-199, 1966. Titanium oxide is not so effective as aluminium oxide with regard to surface area. This area and the volume of

chemisorbed CO normally increase with promoter content, but in contrast to the other promoters (Al_2O_3, MgO, CaO) TiO_2 had a maximum in the volume of chemisorbed CO at about 0.5 g atom cation per 100 g atom Fe.

The main object of the present invention was to develop a catalyst for ammonia synthesis with improved activity.

Higher activity could be utilized in two ways: High reaction rate at high ammonia concentrations or higher activity at low temperatures.
The catalyst activity may be expressed as a rate constant in a rate equation for the synthesis reaction. The rate is a function of temperature, pressure and the composition of the gas, and decreases rapidly with increasing ammonia concentrations. Thus a large fraction of the catalyst volume in a synthesis converter will have ammonia concentration approaching the exit concentration. Hence, to improve the efficiency, increasing the reaction rate at high ammonia concentration is of perticular interest.
As the equilibrium temperature decreases with increasing ammonia concentration, searching higher conversion by increasing the reaction rate at high ammonia concentration also means searching a catalyst with higher activity at low temperature.

The inventors have manufactured a lot of samples of iron oxide based catalysts with various promoters in various concentrations to improve the catalyst activity. In addition to the conventional promoters mentioned above, new promoters have been tested, in particular cobalt- and titanium oxide.

The inventors found that the reaction rate at high ammonia concentration increased with 10-20% when both cobalt- and titanium oxide were used as promoters together with the conventional promoters.

The most preferred catalyst was achieved when the concentration of cobalt was between 0.1% and 3.0 % by weight of metal and when the concentration of titanium was between 0.1 % and 1.0 % by weight of metal.

The atomic ratio Fe^{2+}/Fe^{3+} was between 0.5-0.65.

The present invention will thus in its widest scope comprise a catalyst for the synthesis of ammonia from hydrogen and nitrogen consisting of iron oxides and promoters where the promoters comprise oxides of both cobalt and titanium in addition to Al, K, Ca and Mg oxides.

The invention will be further explained in the example.

Example:

Samples were made by mixing iron ore, mainly magnetite, Fe_3O_4, with promoters. These mixtures were then melted in a ceramic crucible in a laboratory furnace. The temperature was kept at about 1600 °C. The ratio of Fe^{2+}/Fe^{3+} was adjusted to within 0.5 to 0.65 by adding Fe-metal to the melt.
The melt was then poured into an iron crucible and cooled.

The concentration of the promoters in the samples varied as shown in table I:

Table I:

K	0.4 - 0.5
Ca	1.6 - 1.8
Mg	0.3 - 0.5
Al	1.5 - 1.8
Co	0.10- 3.00
Ti	0.14- 0.95

The balance being iron oxides with natural impurities. The cooled samples were crushed and sieved to 0.4 - 0.63 mm particles for testing in a microreactor.

The samples, (10 g each), were tested together with the reference sample in a microreactor. The reference sample was a conventional catalyst with no cobalt- or titanium oxide added.

The samples were reduced in a flow of H_2 and N_2 in the ratio 3/1 at a space velocity of 33000 1 /h. The increase in temperature was 3°C/h from 250°C to 520° C and 520° C was kept for 24 hours to ensure complete reduction.

The samples were then tested at a pressure of 50 bar, space velocity in the range 8000 to 50000 1/h, and temperatures in the range 350°C to 420° C. The inlet gas was H_2/N_2=3/1 with an ammonia concentration of 1.0 to 1.2 % (vol.). Exit ammonia concentration was in the range 4 to 9 % (vol.).

The data obtained during a period of about 100 hours and after an initial stabilisation of 24 hours or more, were used to calculate parameters in a kinetic model for the reaction. The model was then further used for calculating the relative activity and relative reaction rate at higher ammonia concentration than used in the test.

The following table II shows the concentration of cobalt and titanium in the various samples, average relative catalyst activities and predicted relative reaction rate at higher ammonia concentration (20% NH_3, 420°C) calculated by the kinetic model.

Table II:

Sample	Co w %	Ti w %	Average Relative Catalyst Activity at 350°C	Relative Reaction Rate (20% NH_3 and 420°C)	Average Relative Catalyst Activity at 420°C
1 (reference)	0	0.14 (impurity)	1.0	1.0	1.0
2	1.38	0.14 "	1.0	1.06	1.06
3	2.94	0.14 "	1.04	1.08	1.13
4	0.1	0.83	0.91	0.86	0.91
5	0.1	0.4	0.71	0.97	0.93
6	0.1	0.91	1.04	0.91	1.02
7	1.24	0.41	1.08	1.13	1.18
8	0.35	0.38	1.04	1.22	1.13
9	0.56	0.54	1.12	1.22	1.17

Table II shows that the relative reaction rate was highest at high concentration of ammonia (20%) when both cobalt oxide and titanium oxide were added as promoters (compare sample 7-9 with sample 1).

Furthermore, the table II shows that by adding either cobalt oxide or titanium oxide alone, together with the other conventional promoters, a lower relative reaction rate at high concentration of ammonia was obtained (compare samples 2-3 and 4-6 with sample 1).

Furthermore, table II shows that the activity was increased at temperatures down to 350°C when both cobalt- and titanium oxide were added as extra promoters (see sample 7-9).

The example also shows that the activity was increased both at low and high reaction temperature when both cobalt- and titanium oxide were added as promoters.

CLAIMS:

1. A catalyst for the synthesis of ammonia from hydrogen and nitrogen consisting of iron oxides and promoters characterised in that the promoters comprise oxides of both cobalt and titanium in addition to Al, K, Ca and Mg oxides.

2. A catalyst for the synthesis of ammonia from hydrogen and nitrogen according to claim 1, characterised in that, the concentration of cobalt is between 0.1% and 3.0 % by weight of metal and the concentration of titanium is between 0.1% and 1.0% by weight of metal.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO 99/00008

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: B01J 21/06, C01C 1/04
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C01C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0034403 A1 (OZYAGCILAR, MEHMET N.), 26 August 1981 (26.08.81), claim 10, abstract ---	1-2
A	GB 2144336 A (E I DU PONT DE NEMOURS AND COMPANY), 6 March 1985 (06.03.85), page 2, line 1 - line 14 ---	1-2
A	US 3839229 A (MICHEL SENES ET AL), 1 October 1974 (01.10.74), abstract --- --------	1-2

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" erlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 August 1999	12 -08- 1999
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Mårten Hulthén/ELY Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

Information on patent family members

01/07/99

International application No.
PCT/NO 99/00008

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0034403 A1	26/08/81	BR 8100248 A	04/08/81
		JP 56149315 A	19/11/81
		ZA 8100332 A	28/07/82
GB 2144336 A	06/03/85	DE 3428769 A	14/02/85
		US 4480051 A	30/10/84
US 3839229 A	01/10/74	BE 780772 A	18/09/72
		CA 998990 A	26/10/76
		DE 2212358 A	20/09/73
		FR 2129148 A	27/10/72
		NL 7203559 A	19/09/72

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WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
B01J 21/06, C01C 1/04

A1

(11) International Publication Number: WO 99/46038

(43) International Publication Date: 16 September 1999 (16.09.99)

(21) International Application Number: PCT/NO99/00008

(22) International Filing Date: 11 January 1999 (11.01.99)

(30) Priority Data:
19981118 13 March 1998 (13.03.98) NO

(71) Applicant *(for all designated States except US)*: NORSK HYDRO ASA [NO/NO]; N–0240 Oslo (NO).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: FUGLERUD, Terje [NO/NO]; Snarveien 1, N–3925 Porsgrunn (NO). SKAUGSET, Per, Torbjørn [NO/NO]; Borgeåsen Terrasse 15, N–3911 Porsgrunn (NO).

(74) Agent: JOHNSEN, Venche, Høines; Norsk Hydro asa, N–0240 Oslo (NO).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: CATALYST FOR THE SYNTHESIS OF AMMONIA FROM HYDROGEN AND NITROGEN

(57) Abstract

The present invention relates to a catalyst for the synthesis of ammonia from hydrogen and nitrogen consisting of iron oxides and promoters where the promoters comprise oxides of both cobalt and titanium in addition to Al, K, Ca and Mg oxides, and where the concentration of cobalt is between 0.1 % and 3.0 % by weight of metal and the concentration of titanium is between 0.1 % and 1.0 % by weight of metal.

ATTACHMENT A

PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
P9815		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/NO99/00008	11/01/1999	13/03/1998
International Patent Classification (IPC) or national classification and IPC B01J21/06		
Applicant NORSK HYDRO ASA et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 4 sheets, including this cover sheet.

   ☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
04/10/1999	13. 01. 00
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Hoefer, R Telephone No. +49 89 2399 8401

Form PCT/IPEA/409 (cover sheet) (January 1994)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/NO99/00008

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1-6 as published

Claims, No.:

1,2 as published

2. The amendments have resulted in the cancellation of:

☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims 1,2
	No:	Claims
Inventive step (IS)	Yes:	Claims 1,2
	No:	Claims
Industrial applicability (IA)	Yes:	Claims 1,2
	No:	Claims

2. Citations and explanations

s e separate sheet

Re Item V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1.) Reference is made to the following documents:

D1: US-A 3 839 229

D2: S. ABDKADYROVA et al., TR. MOSK. TEKHNOL. INST., no. 2, pages 122-125,(1970) (cited in the application).

2.) The document D1 is regarded as being the closest prior art to the subject-matter of claim 1 and discloses a catalyst for the synthesis of ammonia. The catalyst comprises iron oxides, cobalt oxide and one or more further promoter components selected from the oxides of potassium, aluminium calcium or magnesium (D1: claims 1 and 2).

The subject-matter of claim 1 of the application therefore differs from this known catalyst at least in that it additionally contains titanium oxide.

3.) The catalyst of the invention when used in the ammonia synthesis shows an increased activity at both low and high reaction temperatures.
This is convincingly demonstrated in the examples of the application.

This effect could not be expected from the prior art, in particular because it was known from D2 that titania reduces the activity in ammonia synthesis catalysts.

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference P9815	FOR FURTHER ACTION	see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.
International application No. PCT/NO 99/00008	International filing date *(day/month/year)* 11 January 1999	(Earliest) Priority Date *(day/month/year)* 13 March 1998
Applicant Norsk Hydro ASA et al		

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 2 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. [ ] Certain claims were found unsearchable (See Box I).

2. [ ] Unity of invention is lacking (See Box II).

3. [ ] The international application contains disclosure of a nucleotide and/or amino acid sequence listing and the international search was carried out on the basis of the sequence listing
   - [ ] filed with the international application.
   - [ ] furnished by the applicant separately from the international application,
     - [ ] but not accompanied by a statement to the effect that it did not include matter going beyond the disclosure in the international application as filed.
   - [ ] transcribed by this Authority.

4. With regard to the title,
   - [ ] the text is approved as submitted by the applicant.
   - [X] the text has been established by this Authority to read as follows:

     Catalyst for the synthesis of ammonia from hydrogen and nitrogen.

5. With regard to the abstract,
   - [X] the text is approved as submitted by the applicant.
   - [ ] the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the drawings to be published with the abstract is:

   Figure No. ---
   - [ ] as suggested by the applicant.
   - [ ] because the applicant failed to suggest a figure.
   - [ ] because this figure better characterizes the invention.
   - [ ] None of the figures.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO 99/00008

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: B01J 21/06, C01C 1/04
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C01C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0034403 A1 (OZYAGCILAR, MEHMET N.), 26 August 1981 (26.08.81), claim 10, abstract --	1-2
A	GB 2144336 A (E I DU PONT DE NEMOURS AND COMPANY), 6 March 1985 (06.03.85), page 2, line 1 - line 14 --	1-2
A	US 3839229 A (MICHEL SENES ET AL), 1 October 1974 (01.10.74), abstract -- --------	1-2

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Mårten Hulthén/ELY Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0034403 A1	26/08/81	BR 8100248 A	04/08/81
		JP 56149315 A	19/11/81
		ZA 8100332 A	28/07/82
GB 2144336 A	06/03/85	DE 3428769 A	14/02/85
		US 4480051 A	30/10/84
US 3839229 A	01/10/74	BE 780772 A	18/09/72
		CA 998990 A	26/10/76
		DE 2212358 A	20/09/73
		FR 2129148 A	27/10/72
		NL 7203559 A	19/09/72